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## (54) Crystallizing phosphoric acid

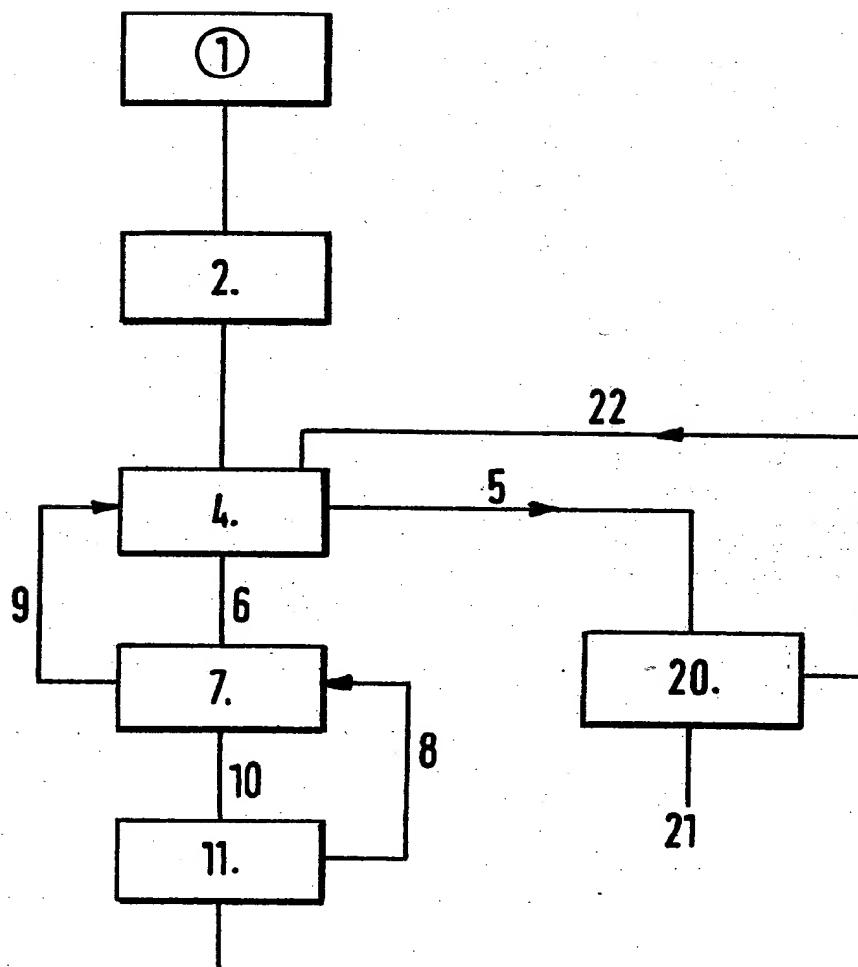
(57) Wet process phosphoric acid containing 64—75% P<sub>2</sub>O<sub>5</sub> and 50—1000 ppm Al and preferably with a total metals content of 0.3—0.7%, e.g. from Nauru rock is crystallized to form purified crystals of phosphoric

acid in its anhydrous or hemi hydrate form. An integrated process with two crystallizations from the mother liquor, recycle of crystals produced to an earlier stage of the crystallization and a recrystallization of the product crystals gives a 60% yield of highly purified acid.

GB 2 078 694 A

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**SPECIFICATION**  
**Purification process**

This invention relates to the crystallization of phosphoric acid.

Phosphoric acid in industry is derived from "thermal" acid which is very pure and made from 5  
 5 elemental phosphorus, or crude wet process phosphoric acid, made from phosphate rock and sulphuric acid. It is known to crystallize thermal phosphoric acid to form crystals of anhydrous or hemihydrate acid, and many people have tried to crystallize wet process acid but very few have been successful and for a number of reasons no commercial process involving crystallization has been operated 5  
 10 commercially for any significant period. The problems with the crystallization result from the impurities 10  
 10 in the acid, which drastically increase the viscosity of the acid making the crystallization difficult to control and making the removal of mother liquor from the crystals difficult. Some of the impurities also tend to cocrystallize with the acid resulting in less purification and in some cases concentration of impurities in the crystals. Purification by crystallization has been described in association with other prior purification techniques i.e. chemical purification as in Jap. Patent 44-14692 or solvent purification 15  
 15 as in BP 1436115 or evaporation to at least 76%  $P_2O_5$  concentration and separation of precipitated impurities, as in OLS 2815880. All these prior purification processes give substantially pure acids containing e.g. less than 1000 ppm total metals before the crystallization stage, so that again only an essentially already pure acid is crystallized. All these purification procedures suffer from disadvantages 20  
 20 of too many stages of different types of procedure leading to uneconomic processes.  
 20 We have now found how to obtain phosphoric acid of substantial purity directly from wet process acid.

The present invention provides a process for preparing purified phosphoric acid, wherein wet process phosphoric acid containing 64—75%  $P_2O_5$  50—1000 ppm Al and preferably 0.01—0.08% Mg, and 0.01—0.8% Ca and 0.01—0.8% Fe is cooled to produce crystals of purified anhydrous or hemi 25  
 25 hydrate phosphoric acid and a mother liquor and the crystals are separated from said mother liquor. Preferably said crystals are recrystallized at least once more e.g. 1—5 more times.

The wet process acid may contain 0.001—0.1% Ca such as 0.01—0.1% Ca e.g. 0.01—0.05% Ca, 0.01—0.6% Mg such as 0.1—0.5% Mg such as 0.1—0.35% Mg, 0.01—0.8% Fe e.g. 0.01—0.5% Fe such as 0.1—0.3% Fe, 50 ppm—1000 ppm Al e.g. 50—500 ppm Al, 0.01—0.8% F such as 30  
 30 0.01—0.4% F e.g. 0.01—0.2% F and 1—3%  $SO_4$  or less than 1%  $SO_4$  e.g. 0.01—0.5% such as 0.1—0.5%  $SO_4$ . The acid may contain 0.01—0.8% Zn such as 0.01—0.2% Zn, as well as other impurities such as Cr, Ti, Si, Mn, Na usually in individual amounts of less than 800 ppm usually less than 200 ppm each and a total of less than 0.2%. Preferably the acid contains less than 1% of total metals e.g. 0.1—1% such as 0.3—0.85% especially less than 0.7% such as 0.3—0.7% total metals. Preferably 35  
 35 the acid contains less than 0.1% organics (expressed as carbon) e.g. 1—500 ppm organics.

The wet process acid is usually derived from calcined phosphate rock particularly Nauru phosphate rock after calcination e.g. at 750—1000°C to remove its organics and sometimes its carbonate content and reduce its F and Si content. Alternatively calcined phosphate rock from Zin in Israel Youssoufia, Khouribga, Bu Craa and Jordan may be used. The rock is treated with a mixture of 40  
 40 sulphuric and phosphoric acid to form calcium sulphate and wet process acid, which are separated. The wet process acid is then concentrated e.g. from the 28—50%  $P_2O_5$  acid made from the rock. The concentration may be by high temperature evaporation e.g. by vacuum evaporation to give 64—68%  $P_2O_5$  acid or by submerged combustion or by evaporation by direct electrical heating, using the electrical cell as described in OLS 2815880. Any solids e.g. calcium sulphate separating during or after 45  
 45 the concentration are removed before the crystallization. Advantageously the acid is concentrated to an intermediate level of concentration e.g. 50—68%  $P_2O_5$  by e.g. vacuum evaporation and then concentrated further if needed e.g. by the direct electrical heating process. Usually the crystallization is carried out directly on the product of concentrating the wet process acid made directly from the rock calcined or otherwise with no extra purification steps to remove cation impurities (and preferably no 50  
 50 extra purification steps to remove anion impurities) apart from separation of any solids forming during or after the concentration and of course separation of the solid comprising calcium sulphate in the production of the wet process acid. Thus preferably no solvent treatment is carried out to precipitate or otherwise remove impurities or to separate acid into an organic phase from which acid is recovered, and no addition of reagents causing precipitation of impurities in the wet process acid before, during or after 55  
 55 concentration. The concentration of the wet process acid is raised to a level not greater than 75%  $P_2O_5$ .

The wet process acid of 64—75%  $P_2O_5$  concentration is agitated and cooled, preferably with addition of seed crystals of purified phosphoric acid or thermal phosphoric acid. The acid is cooled to a temperature usually 3—40°C e.g. 10—40°C less than the melting point of phosphoric acid of that  $P_2O_5$  concentration; the crystallization temperature is lower the lower the  $P_2O_5$  content of the acid and 60  
 60 the higher the total metal impurity content. For 72% acid the acid is usually cooled to 0—40°C and for 66%  $P_2O_5$  acid the acid is usually cooled to —20° to +15°C. The wet process acid preferably has a concentration greater than 72.4%  $P_2O_5$  if anhydrous acid is wanted though acids of 68—75%  $P_2O_5$  e.g. 70—75% may be used for this purpose or 66—68%  $P_2O_5$  if hemi hydrate acid is wanted. The crystallization is advantageously completed in 0.1—10 hr e.g. 0.3—2.0 hr. The magma is then

3 70—75%  $P_2O_5$  acid) often need recrystallization only once while those from corresponding acids with 0.4—0.8% Mg or 0.4—0.6% Mg (again e.g. for a 70—75%  $P_2O_5$  acid) are often recrystallized twice to give similar purity acids. Advantageously the mother liquor from the or each recrystallization is recycled to the previous crystallization stage.

In order to maximize the yield of purified acid, it is preferable to take an initial crop of crystals 10 containing 30—70% of the  $P_2O_5$  in the acid being crystallized and then recover further successive crops of crystals from the mother liquor, preferably 1 or 2 such further crops. Each successive crop of crystals is preferably remelted and mixed with the mother liquor from the previous crystallization. Preferably also each crystallization stage is operated to give 30—70% e.g. 45—65% of the  $P_2O_5$  in the acid which is crystallized being recovered as crystals. Thus in an integrated process a concentrated wet process acid 15 is separated into two fractions, one highly purified acid, which is two or three times crystallized, and an impure mother liquor from which 2 or 3 successive crops of crystals have been removed.

Preferably in the process, the crude acid is crystallized and separated into first purified crystals and a first mother liquor, which are separated, the first mother liquor is cooled further to produce second purified crystals which are separated from second mother liquor, said second purified crystals are 20 melted to give a second acid which is mixed with the crude acid before crystallization, the first purified crystals are melted to give a first acid and the acid cooled to give third purified crystals which are separated from a third mother liquor, which is recycled to mix with the crude acid before crystallization, in each of the 3 crystallizations 30—70% of the  $P_2O_5$  values in the liquid acid being separated as crystals; advantageously the third purified crystals are melted to give a third acid which is cooled to give 25 fourth purified crystals which are separated from a fourth mother liquor which is recycled to mix with the first acid before the crystallization of the third purified crystals.

While it is possible to obtain two successive crops of crystals from the mother liquor from the first crystallization, we have found that with some acids solids in particular a magnesium dihydrogen phosphate-phosphoric acid complex tends to be deposited easily in the second successive 30 crystallization from the mother liquor and with difficulty and slowly in the first successive crystallization. This problem becomes important when the Mg content of the acid being crystallized at that stage reaches 7700 ppm (e.g. for a 68—75%  $P_2O_5$  acid). With original acids of 64—75%  $P_2O_5$  content from which the first crystals were obtained in which the Mg content of the original acid was above 0.4%, one successive crystallization only is desirable and that should be done quickly within 3 hr; the original acids 35 with Mg contents of up to 0.4% e.g. 0.1—0.35% Mg (e.g. for a 70—75%  $P_2O_5$  acid) as in acid from calcined Nauru rock can be submitted to the two successive crystallizations from the mother liquor usually without such deposition problems, at least when yields of 30—60% of crystals are taken at each stage.

Final decolourization of the purified acids from the effects of any residual organic impurities may 40 be carried out if needed or desired by treatment with activated carbon. In this way water white acid may be obtained by twice crystallization from the green crude acid.

Advantageously the invention is carried out as shown in the accompanying drawing which is a block diagram of an integrated process for converting dilute wet process acid into purified crystalline anhydrous acid.

45 Dilute wet process phosphoric acid 1 is concentrated e.g. in an electrically heated graphite cell in 2 and the concentrated acid filtered if necessary to remove precipitate. The filtered concentrated acid is mixed with melted recrystallized acid 9 and mother liquor 22 from a recrystallization of the crystals first produced. The concentrated acid at 4 is cooled, seeded and allowed to crystallize to give crystals 5 and mother liquor 6, which are separated. Mother liquor 6 is mixed at 7 with melted crystals 8, cooled 50 further, reseeded, and a further crop of crystals 9 is obtained with mother liquor 10; the crystals 9 and mother liquor 10 are separated. Crystals 9 are melted and passed to the initial crystallization stage while mother liquor 10 is cooled and seeded at 11 to give a further crop of crystals 8 and mother liquor 12, which are separated. Crystals 8 are melted and recycled to 7 while mother liquor 12 may be converted into fertilizers or industrial phosphates such as tripolyphosphates.

55 First crop crystals 5 are remelted and cooled and crystallized at 20 with addition of seed crystals of purified acid to give further purified crystals 21 and mother liquor 22 which is recycled to the first crystallization 4. The purified crystals 21 may be used in metal finishing solutions, or even in food, depending on their impurity content. The purified crystals may, in a process not shown, be melted, cooled and crystallized again to give trebly purified crystals, which are separated, the mother liquor 60 being recycled to the first recrystallization at 20.

The invention is illustrated in the following Examples in which percentage are by weight. The crude acid for Ex. 1 and 2 was obtained as follows. Nauru apatite phosphate rock was calcined at 850°C to give a calcined rock, which was then treated with a mixture of sulphuric and phosphoric acids containing sulphuric acid in amount to react with 98% of the Ca content of the rock, to give gypsum and 65 wet process acid which were separated. The wet process acid contained 33.4%  $P_2O_5$ , 0.51%  $SO_4$ .

0.31% F, 0.13% Fe, 0.13% Mg, 0.17% Ca, 680 ppm Na, 290 ppm Zn, 110 ppm Al, 13 ppm Cl, 55 ppm K, 170 ppm Si as well as other metallic and non metallic inorganic impurities in total amount of less than 300 ppm and less than 25 ppm organic impurities (expressed as carbon).

The wet process acid was concentrated by evaporation by direct electrical resistance heating in a 5 cell as described in OLS 2815880, to give a concentrated acid containing 73.0%  $P_2O_5$ , 0.22% Fe, 0.21% Mg, 640 ppm Zn, 190 ppm Ca, 96 ppm Al, 140 ppm Cr, 0.0785% F, 0.26%  $SO_4$ , 5.4 ppm As and other metallic and non metallic impurities in amount of less than 700 ppm. A small amount of solids were separated from the hot concentrated acid.

The warm filtered concentrated acid was placed in a crystallizer fitted with paddle stirrer and 10 cooled to 35°C. Seed crystals of purified anhydrous phosphoric acid were added and after further cooling to 30°C over 45 min, the crystals which had formed were separated from the magma in a centrifuge to give a 50% recovery of crystalline anhydrous phosphoric acid containing 380 ppm Fe, 350 ppm Mg, 88 ppm Zn, 60 ppm Ca, 39 ppm Al, 25 ppm Cr, 180 ppm F, 340 ppm  $SO_4$  and 0.9 ppm As.

15 The crystalline anhydrous acid obtained was melted and crystallized to 34°C with added seed crystals of purer acid to give a magma from which centrifugation gave a 50% recovery of recrystallized anhydrous phosphoric acid containing 39 ppm Fe, 36 ppm Mg, 10 ppm Zn, 10 ppm Ca, 2 ppm Al, 4 ppm Cr, 35 ppm F, 40 ppm  $SO_4$  and 0.2 ppm As.

20 Two further crops of crystals were obtained from the mother liquor from the crystallization of the concentrated acid in amounts (expressed as recovery of crystals as a percentage of original concentrated acid) and with purities (in ppm) as given below. The crystallization conditions of temperature and time were 30°C for 50 min for the second crop and 15°C for 100 min for the third crop.

	Crop	Recovery %	Fe	Mg	Zn	Ca	Al	Cr	F	As	$SO_4$	
25	Second	25	1500	1400	350	260	52	82	435	5.3	1500	25
	Third	12.5	4100	3800	1000	270	180	250	410	10.6	5100	

#### EXAMPLE 2

An integrated crystallization process was carried out with process operations as shown in the accompanying drawing. The initial concentrated acid was as described in Example 1 and was mixed 30 with remelted crystals from the second crystallization of mother liquor and with mother liquor from the recrystallization of the crystals from the first crystallization. The crystallization temperature for the first crystallization was 36°C and the crystallization time was 40 min. Other crystallization temperatures and times were as described in Ex. 1. In each case seed crystals were added. A 50% split of  $P_2O_5$  between the crystals and mother liquor at each stage was performed. A total recovery of 60% of twice purified 35 crystals of anhydrous phosphoric acid was obtained. Analyses of the twice purified crystals (21) and the residual mother liquor (from 11) were as follows (in ppm).

	Fe	Mg	Zn	Ca	Al	Cr	F	As	$SO_4$
Crystals	13	12	3	3	<1	<1	12	<0.1	13
Mother Liquor	5485	5237	1595	470	240	350	1945	15	6480

#### 40 EXAMPLE 3

In a similar manner to that of Ex. 1, a wet process acid was made from calcined Zin (Israel) rock, concentrated and any solids separated, then crystallized once at a 50% split of crystals to mother liquor, the crystals remelted and recrystallized again with a 50% split of crystals to mother liquor and the original mother liquor cooled and crystallized again. Analyses of the various fractions (amounts being expressed in part per million by weight apart from the  $P_2O_5$  value) were as follows.

	Acid	% $P_2O_5$	Fe	Mg	Zn	Ca	Al	Cr	F	$CO_2$
1		71.2	1400	4600	920	47	140	200	2270	20600
2		72.3	380	1000	240	40	40	62	740	5700
3		73.4	45	71	11	2	3	8	280	1000
50	4	70.7	1400	7700	1100	96	150	210	2130	28400
	5	66.3	3200	7400	1800	36	290	430	3430	37600

The crystallization times and temperatures were similar to those in corresponding stages of Ex. 1 but generally 1—5°C lower. In this table acid 1 is the crude concentrated acid, acid 2 is the first crystals, acid 3 is recrystallized acid from those crystals, acid 4 is the crystals from the first mother liquor and acid 5 is the second mother liquor from the crystallization of acid 4.

### 5 EXAMPLE 4

An identical operation to that of the process of Ex. 3 was performed with wet process acid made from calcined Youssoufia phosphate rock apart from a double recrystallization of the crystals of acid first obtained under conditions similar to those of the first crystallization in Ex. 3. The results were as follows, analyses expressed being expressed as in Ex. 3.

10	Acid	%P <sub>2</sub> O <sub>5</sub>	Fe	Mg	Zn	Ca	Al	Cr	F	SO <sub>4</sub>	10
	1	70.1	2000	4200	1100	74	160	570	2300	25700	
	2	72.0	550	1000	270	51	40	170	780	5800	
	3	71.7	54	100	22	15	4	24	311	725	
	4	72.0	2	11	<2	3	<1	5	30	60	
15	5	69.0	2480	5145	1300	25	140	600	2300	33250	15
	6	65.0	5320	10050	2900	40	420	1300	2500	53350	

In this table acid 1 is the concentrated acid, acid 2 is first crystals, acid 3 is the recrystallized acid from those crystals, acid 4 is the acid obtained by crystallization of the melted acid 3, acid 5 is the crystals from the first mother liquor and acid 6 is the second mother liquor from the crystallization of acid 5.

### 20 CLAIMS

1. A process for preparing purified phosphoric acid, wherein crude wet process phosphoric acid containing 64—75% P<sub>2</sub>O<sub>5</sub> and 50—1000 ppm aluminium (expressed as Al) is cooled to produce crystals of purified anhydrous or hemihydrate phosphoric acid and a mother liquor, and the crystals are separated from said mother liquor.
2. A process according to claim 1 wherein the wet process acid contains 0.01—0.8% Mg.
3. A process according to claim 2 wherein the wet process acid contains 0.1—0.5% Mg.
4. A process according to claim 3 wherein the wet process acid contains 68—75% P<sub>2</sub>O<sub>5</sub> and 0.1—0.35% Mg.
5. A process according to any one of claims 1—4 wherein the wet process acid contains 0.01—0.8% calcium (expressed as Ca) and 0.01—0.8% iron (expressed as Fe).
6. A process according to any one of claims 1—5 wherein the wet process acid contains 50—500 ppm Al.
7. A process according to any one of claims 1—6 wherein the wet process acid contains 0.3—0.7% total metals (expressed as their elements).
8. A process according to any one of claims 1—7 wherein the separated crystals are melted and recrystallized to produce a recrystallized purified acid, which are separated from a second mother liquor.
9. A process according to claim 8 wherein the second mother liquor is recycled to the initial crystallization.
10. A process according to claim 9 wherein the crude acid is crystallized and separated into first purified crystals and a first mother liquor, which are separated, the first mother liquor is cooled further to produce second purified crystals which are separated from second mother liquor, said second purified crystals are melted to give a second acid which is mixed with the crude acid before crystallization, the first purified crystals are melted to give a first acid and the acid cooled to give third purified crystals which are separated from a third mother liquor, which is recycled to mix with the crude acid before crystallization, in each of the 3 crystallizations, 30—70% of the P<sub>2</sub>O<sub>5</sub> values in the liquid acid being separated as crystals.
11. A process according to claim 10 wherein the third purified crystals are melted to give a third acid which is cooled to give fourth purified crystals which are separated from a fourth mother liquor which is recycled to mix with the first acid before the crystallization of the third purified crystals.
12. A process according to any one of claims 1—11 wherein the crude acid has been made by acidification of phosphate rock, separation of calcium sulphate from a phosphoric acid which is concentrated in at least one step and any insoluble solids separated.
13. A process according to claim 12 wherein the crude acid for crystallization has been made from a dilute phosphoric acid by concentration without any extra purification steps involving addition of any precipitating reagents or any organic solvent.

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14. A process according to any one of claims 1—13 wherein the crude acid is derived from calcined Nauru rock.
15. A process according to claim 1 substantially as described in any one of the Examples.
16. Purified phosphoric acid prepared according to any one of claims 1—15.

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